DENSITY AND CRYSTALLIZATION TEMPERATURE OF LITHIUM-BROMIDE AQUEOUS SOLUTION

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ABSTRACT

Lithium-bromide aqueous solution for absorption air-conditioning systems was examined in detail about its densities and crystallization temperatures. The vibratory density meter with U-shaped tube was used for this highly precise experiment. A total of 39 density data was obtained for the concentration of 65.4, 66.2, 67.1, 68.2 and 69.5wt% LiBr for the temperature range of 333 ~ 423 K. A density correlation was made using obtained data. The correlation reproduces the measurement densities ±0.17%. And a total of 8 crystallization temperatures were measured in the range of concentration 65.4 ~ 69.5wt%.

1. INTRODUCTION

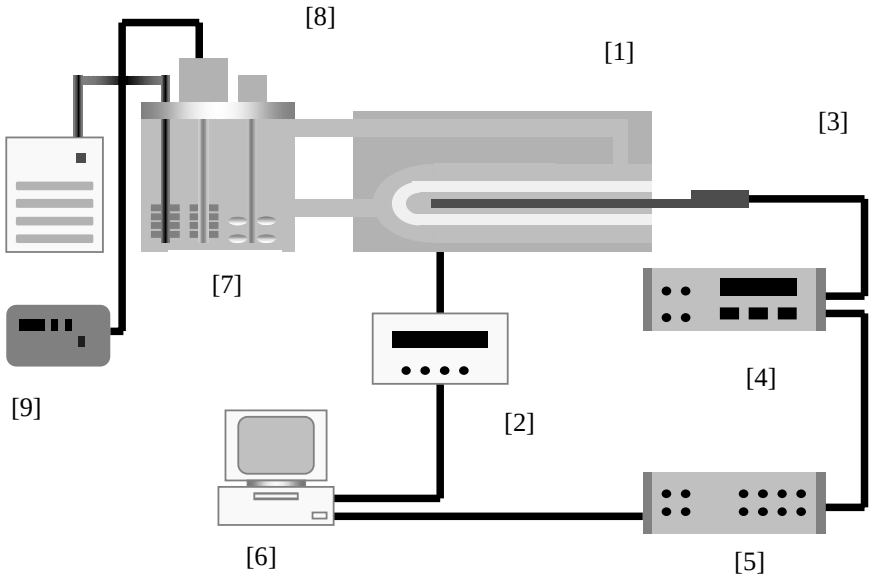
Lithium-bromide aqueous solution is used as a working fluid for absorption air-conditioning systems widely. Because the lithium-bromide is nonvolatile matter, this fluid causes no ozone depletion and global warming. And this human-friendly and earth-friendly substance is expected its popularization. Absorption systems are driven by heat not electric power different from compression systems. From now on, small power generation systems like fuel sells or micro gas turbines must become popular, surplus heat will generate from these systems and absorption systems will be used in these cases as co-generation systems. For these reasons, interests in the absorption systems have been increasing.

For development of advanced cycles or improvements in energy efficiency, high accuracy thermodynamic properties data of working fluids are highly desirable. But in the range of high concentration, measurement data of density and crystallization temperature for the lithium-bromide aqueous solution is limited.

Thus attempts had been made aiming precise measurements of density and crystallization temperature for the lithium-bromide aqueous solution in the range of high concentration.

In this study, results of density and crystallization temperature for the lithium-bromide aqueous solution are presented. A total of 39 density data was obtained for the concentration with 65.4, 66.2, 67.1, 68.2 and 69.5wt% LiBr for the range of temperature 333 ~ 423 K. And a total of 8 crystallization temperatures were measured in the range of concentration 65.4 ~ 69.5wt%.

2. DENSITY MEASUREMENT APPARATUS



[1]Density measuring cell [2]Density meter [3]Sheathed Platinum resistance thermometer [4]Thermometry bridge [5] Standard resistor [6] Computer [7] Thermostat controlled Circulatory bath [8] Stirrer [9] Temperature control unit [10] Cooler

Figure1. Density measurement apparatus

Figure1 shows the density measurement apparatus. This apparatus is composed of three blocks which are density measurement system, temperature measurement system and temperature control system.

Density measurement system is composed of the density measuring cell and the density meter [1, 2] (Anton Paar, Model DMA 602 HTP). Numbers in a bracket represent parts numbers shown in Figure 1. This density meter uses vibratory measuring method because it can measure liquid or gas phase density accurately. The density measuring cell has a vibrating U-shaped sample tube which is filled with sample gas or liquid. The density of the sample will be calculated from measuring the natural period of the sample tube. This method with the vibratory density meter is the most precise

method for gas or liquid density measurement.

The temperature measurement system is composed of the sheathed platinum resistance thermometer [3], the thermometry bridge [4] (Automatic Systems Laboratories, Model F300) and the standard resistor [5]. The 100 Ω sheathed platinum resistance thermometer calibrated against the International Temperature Scale (ITS-90) is measured temperatures of the U-shaped sample tube located in the density measuring cell. Thermometry bridge measures resistance ratio between the sheathed platinum resistance thermometer and the standard resistor.

The temperature control system is composed of the thermostat controlled circulatory bath [7], the stirrer [8], the temperature control unit [9] and the cooler [10]. The U-shaped sample tube is kept at a constant temperature level by heat-transfer fluid supplied from the thermostat controlled Circulatory bath [13].In this experiment, water or silicon oil was chosen as the heat-transfer fluid, depending on the temperature level. Silicon oil is used over 330K and water is used below 330K as the heat-transfer fluid. Temperature in the thermostat controlled circulatory bath is controlled by the temperature control unit. During measurements below 330 K, the cooler [10] was used for temperature control. Thermostat controlled circulatory bath temperature is maintained at the prescribed temperature within ±10mK during experiments

3. CALIBRATION AND MEASUREMENT ACCURACY

3.1 Calibration of the density meter

The vibratory density meter measures the natural period of the vibrating U-shaped sample tube that is filled with sample liquid or gas. The relation between the natural period τ and the density ρ is described by the following equation.

$$\rho=a_0(\tau^2-a_1) \qquad (1)$$

In the equation, a_0 and a_1 are constants inherent to the instrument. These constants are determined by measuring two pair of the natural period of the tube filled with a gas or liquid whose density is known. Vacuum and mercury were chosen as reference fluids for the calibration of the vibratory density meter. A vacuum was achieved to 0.9mPa by using the turbo-molecular vacuum pump. And reagent mercury with 99% in purity was adopted in this calibration. The natural period were measured covering 330~423 K for vacuum and mercury. The constants a_0 and a_1 were determined as a function of temperatures for the range of 0~13500kg/m^3.

Accuracy of density was determined by comparison of experimental water density data by MURAKAMI(2002) with calculated density, which was calculated by using the

internationally recommended IAPWS correlation (1986). On the calibration result, the experimental uncertainty of density is better than 0.5kg/m^3.

3.2 Accuracy of the temperature

The sheathed Platinum resistance thermometer was examined at the triple point and comparison with a standard platinum resistance thermometer. On the calibration result, the experimental uncertainty of temperature is ±0.02K for the range of 273~423K.

3.3 Accuracy of the concentration

Lithium-bromide hydrate ($LiBr \cdot H_2O$) with 99.5% in purity as a reagent and distilled and deaerated water were blended and used for the sample. The concentration of the sample was measured after making it, because the reagent of lithium-bromide hydrate absorbed steam in the air already. A precision electric balance within the uncertainly of ±1mg was used by measuring the concentration. On the scatter of measurement data, measurement accuracy of concentration was determined ±0.5kg/m^3 for the range of 65.4~69.5 wt%.

Measurement accuracy and its coverage of temperature, density and concentration are shown in Table1.

Table1. Measurement accuracy and its coverage

Temperature[K]	Accuracy ±0.02 Coverage 273~423
Density[kg/m^3]	Accuracy ±0.5 Coverage 0~13600
Concentration[wt%]	Accuracy ±0.15 Coverage 65.4~69.5

4. DENSITY OF LITHIUM BROMIDE AQUEOUS SOLUTION

4.1 Density measurement result

In this study, a total of 39 densities have been measured for lithium-bromide aqueous solution with different concentration of 65.4, 66.2, 67.1, 68.2 and 69.5wt% for the range of temperature 333~423 K by using the density measurement apparatus. Figure2 shows distribution of experimental densities of lithium-bromide solution. In the figure, density is shown in the vertical axis and temperature is shown horizontal axis.

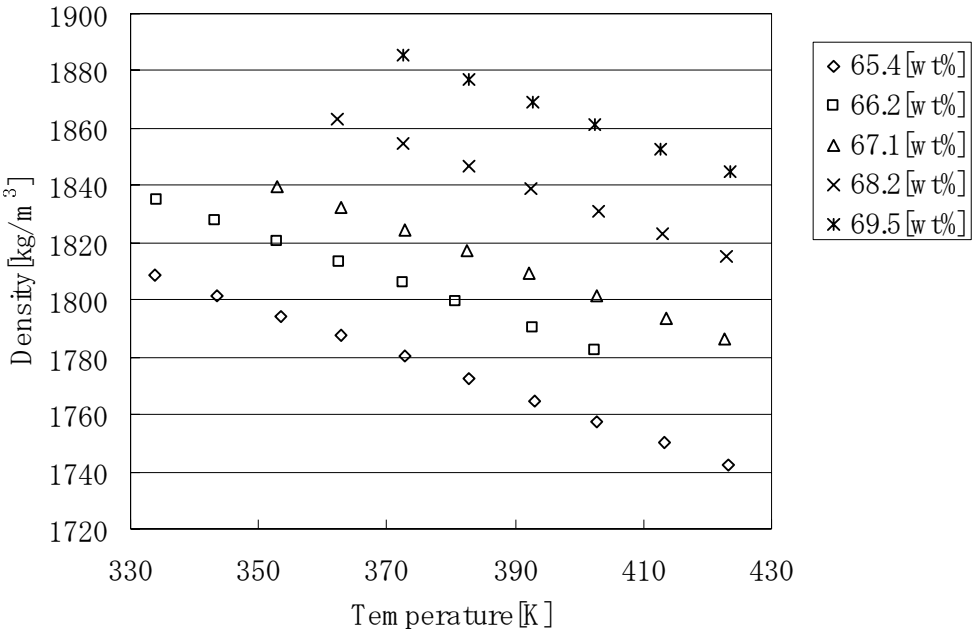


Figure2. Distribution of experimental densities of lithium-bromide solution

4.2 Density correlation of Lithium-bromide aqueous solution

The density is almost proportional to temperature. Thus, the density ρ can be approximated as a linear function of the temperature T. A correlation between the density, temperature and concentration of lithium bromide aqueous solution was derived from the present measurements. The correlation is shown in the following.

$$\rho = A_1 T + A_2$$
$$A_1 = -0.014396x + 0.19405, \quad A_2 = 30.723x + 51.718 \qquad (2)$$
$$333 < T < 430, \quad 65 < x < 70$$

where x denotes the weight concentration of LiBr in lithium-bromide aqueous solution in wt%, T is the temperature in K.

Figure3 shows the relative percentage deviations of the measurement densities from the proposed correlation.

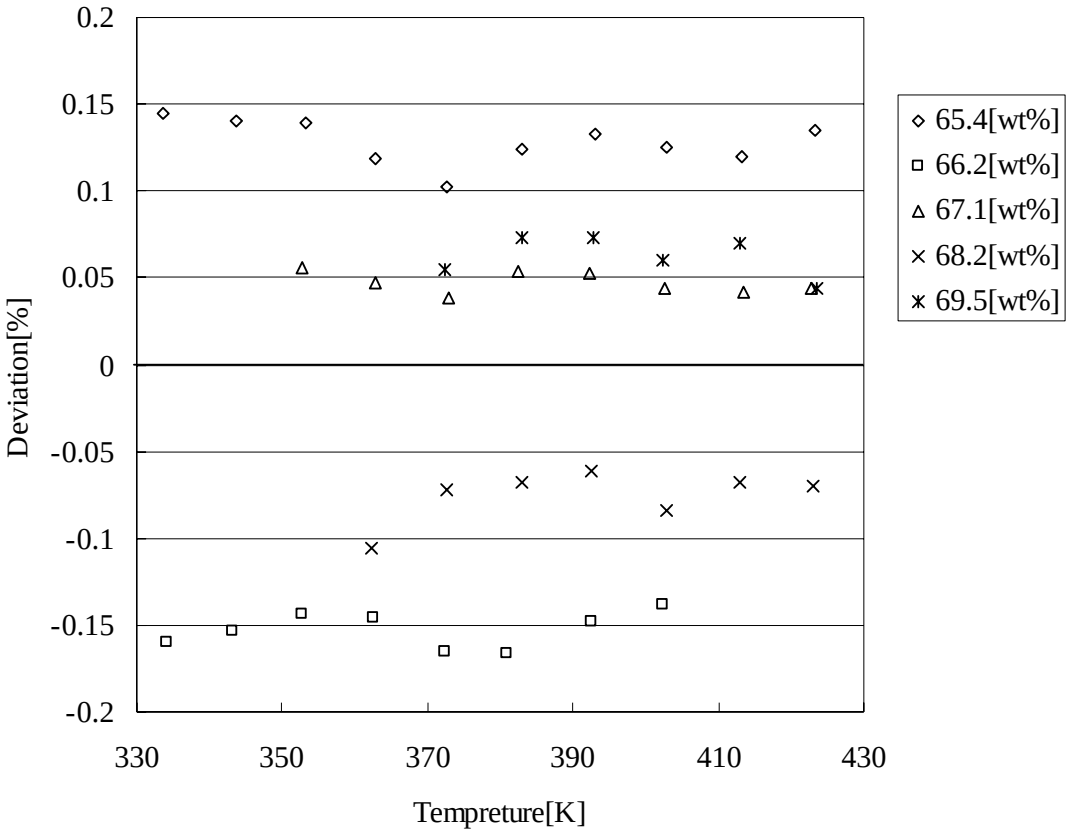


Figure3. Relative deviations of the measurement densities from the correlation

In this figure, relative deviations of the present data from the present correlation are shown in the vertical axis and temperature in the horizontal axis. The greatest deviation is about -0.17% in 66.2 wt% LiBr. The correlation reproduces the measurement densities ±0.17%.

5. CRYSTALLIZATION TEMPERATURE OF LITHIUM-BROMIDE AQUEOUS SOLUTION

The crystallization temperature was measured by using the Density measurement apparatus. The crystallization temperature was determined at the point of a sudden change of the temperature and the natural period of the vibratory density meter as the temperature reduced slowly. The cooling temperature rates were 1~3mK/s depending on the temperature level. At the beginning of crystallization, the temperature begins to rise suddenly because solidification heat generate. In the same time, the period begins to rise. Figure4 shows a change of temperature and natural period with crystallization by way of example.

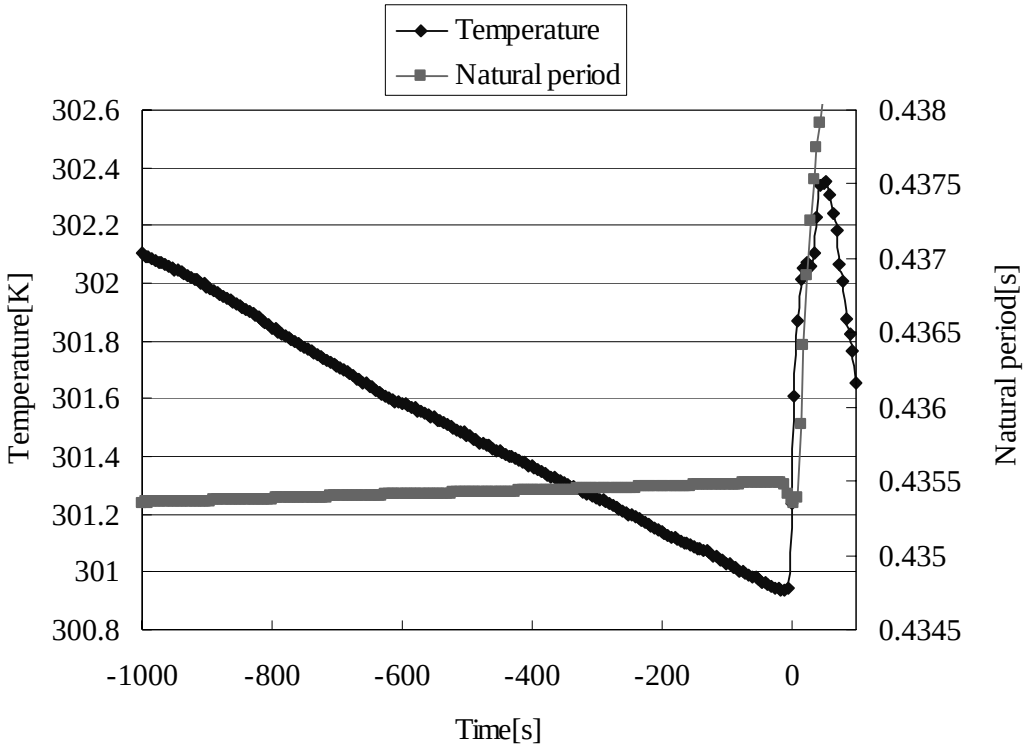


Figure4. Temperature and natural period

In this study, a total of 8 crystallization temperatures have been measured with concentration range of 65.4～69.5wt%. This

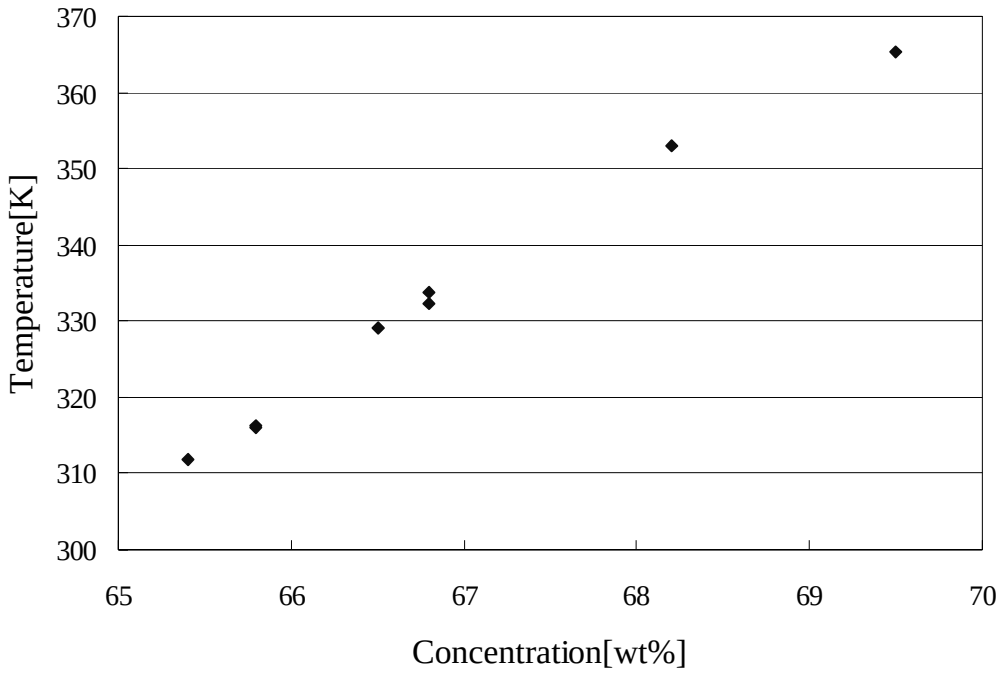


Figure5. Crystallization temperatures

6. CONCLUSION

We have reported a set of measured data regarding the densities of the lithium-bromide aqueous solution for the range of temperature 330~423 K and of concentration 65.4~69.5 wt% LiBr. These experimental data were obtained by using the vibratory density meter, and confirmed the reliability by measurements of water densities. The uncertainly of the density measurements of lithium-bromide aqueous solution would not be greater than ± 0.5 kg/m^3. These obtained densities were correlated as a formula depending on the temperature and the concentration. The correlation reproduces the experimental densities ±0.17%.

The crystallization temperatures were also measured in the range of concentration 65.4~69.5 wt% LiBr. A total of 8 crystallization temperatures have been measured using the experimental apparatus.

REFERENCES

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